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09/882,566	06/15/2001	Paul George Wright	18-468-9-1	1466
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Please find below and/or attached an Office communication concerning this application or proceeding.

KOLTHOFF, LEE,

It was not suitable for polystyrene determinations in low-conversion GR-S and in highconversion GR-S containing small amounts of polystyrene.

An attempt was then made to make use of the fact, noted in this laboratory, that the solubility of GR-S in a mixture of benzene and acctone is small, whereas polystyrene is freely soluble in such mixtures. For example, in a mixture of 80% acetone and 20% benzene, varying amounts of a low-conversion (24%) GR-S sample prepared by bottle polymerization, were almost completely separated from high-conversion (80%) polystyrene. To 20 ml. of benzene solutions containing varying ratios of high-conversion polystyrene and low-conversion GR-S in a total concentration of 1%, 80 ml. of acetone was added. The precipitated GR-S polymer was filtered off and was found to contain about 1% polystyrene (from a determination of the iodine number). The filtrate was then added to a large volume of ethanol to precipitate the remaining copolymer and polystyrene. The amounts of polymer found in this second precipitation are given in Table I.

separation of 24%-conversion or-8 and high-conversion polystyrene IN BENZENE-ACETONE (20:80)

GR-S in original mixture, %	Polystyrene la edginal mixture, %	Polymer net precipitated in 20:30 benzoue-acctone, %	
100	0	1.8	
95	5.	5.8	
75	25	25.5 24.8	
50	- 50	48.0 47.8	

The results summarized in Table I and those of other experiments have shown, however, that the use of a benzene-acetone mixture is not suitable for a quantitative separation of GR-S from polystyrene. The reason is that GR-S contains low molecular weight fractions which are soluble in the benzene-acetone mixture. The principle of separation is mentioned here because it allows a fairly close separation of the GR-S from polystyrene without affecting either substance chemically.

The following procedure describes a possible method for the quantitative determination of polystyrene in GR-S based on the above separation. Collect quantitatively and weigh the GR-S fraction which precipitates when acetone is added to a benzene solution of the sample. This fraction is practically free of polystyrene. Precipitate the remaining copolymer and polystyrene in the benzene solution by the addition of ethanol, and weigh. From the weight of both precipitates and the unsaturation of both fractions (iodine monochloride method), the polystyrene content of the original sample can be calculated.

This method was abandoned in favor of a much simpler procedure which is described below. In brief, the new method is based upon the principle that polymer molecules (such as GR-S) containing ethylenic bonds, when dissolved in benzene, can be broken into fragments by a hydroperoxide in the presence of osmium tetroxide; polymer molecules (such as polystyrene) containing no ethylenic bonds remain unattacked. The

DETERMINATION OF POLYSTYRENE IN GR-S RUBBER

small fragments (aldehydes of low molecular weight) are soluble in ethanol, whereas the unattacked polystyrene is insoluble. Separation of the polystyrene, therefore, consists merely of pouring the reaction mixture (after breakdown of the polymer containing unsaturated groups) into ethanol and filtering off the polystyrene.

It is expected that the oxidation of GR-S described in this paper may be of greater importance in connection with a study of the structure of the copolymer. A quantitative determination of all the oxidation products should give complete insight into the structure. of GR-S and other polymers containing unsaturated bonds. The method appears to have definite advantages over degradation by ozone. This problem will be studied further by H. A. Laitinen of the University of Illinois.

In a subsequent paper we shall describe the reactivity of polymers containing unsaturated groups with perbenzoic acid in an organic solvent and also with perbenzoic acid in the presence of a small amount of osmium tetroxide. With perbenzoic acid alone the double bonds form an oxirane ring (i.e., an epoxide) whereas in the presence of osmium tetroxide, oxidation to aldehydes occurs. Several analytical applications of these reactions will be described later.

REAGENTS

lerl-Butyl Hydroperoxide. A mixture containing 60% tert-butyl hydroperoxide and 40% tert-butyl alcohol was obtained from Union Bay State Company, Cambridge, Massachusetts. The mixture is stable for at least several months at room temperature.

Osmium Tetroxide Solution. 0.08 g. of osmium tetroxide was dissolved in 100 ml. of reagent-grade henzene. The solution is stable for several months if protected from light. Decomposition is indicated by the formation of a black precipitate, osmium sesquioxide or osmium dioxide.

PROCEDURE

Heat 40-50 g. of p-dichlorobenzene contained in a 125-ml. Erlenmeyer flask to 50-60°C. Weigh out a 0.5 to 0.6-g, sample of polymer occurately to 1 mg, and transfer it to the flask. Heat the solution to about 130°C, and maintain the temperature until the sample has dissolved. Even polymers containing gel are dissolved by this procedure. If the sample contains no gel, it will dissolve in 15-30 minutes. A hot plate, not an open flame, should be used to heat the solution. If a flame is used, the polymer will stick to the bottom of the flask due to the high temperature of the glass surface.

Cool the solution to 80-90°C. and add 10 ml. of 60% lert-butyl hydroperoxide. Add 1 ml. of 0.003 M osmium tetroxide solution in benzene. Heat the solution to 110-115°C. and keep at this temperature for 10 minutes. The solution should be perfectly clear at this point.

Cool the solution to 50-60° and add 20 ml. of benzene. Pour the solution slowly into 250 ml. of ethanol containing a few drops of concentrated sulfuric acid. Stir the mixture by means of a mechanical stirrer during this addition. Wash the flask with small portions of benzene. Stir the mixture until the polystyrene has coagulated and the solution is clear. If necessary, the solution should be allowed to stand overnight.

- ³ R. Criegeo, Ann., 522, 75 (1936).
- N. A. Milas and S. Suseman, J. Am. Cham. Soc., 50, 1302 (1986); ibid., 59, 2345 (1937).
- N. A. Miles and S. A. Harris, ibid., 60, 2434 (1988).

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claims recite that the valve is closed automatically as the needle is withdrawn. See e.g. patented claim 1. It is evident, therefore, that the instant claim language is fully anticipated by the patented claims and differs only nominally therefrom.

- 3. The prior art made of record and not relied upon is considered pertinent to applicant's disclosure for the same reasons applied in the parent applications.
- 4. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Jeffrey R. Snay whose telephone number is (703) 308-4032. The examiner can normally be reached on Mon-Fri.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Jill A. Warden can be reached on (703) 308-4037. The fax phone number for the organization where this application or proceeding is assigned is (703) 872-9306.

Any inquiry of a general nature or relating to the status of this application or proceeding should be directed to the receptionist whose telephone number is (703) 308-

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TABLE III
DETERMINATION OF POLYSTYRENE IN PLANT SAMPLES

Delman	Conversion, %	Polystyrene found, %	
Polymor		By camium totroxide method	By iodine mono chloride method
17 P 35 A 2-b 17-P 42 A 1-b Blend B-f 17 P 41 A 2-b	12 12 72 16	0.3 2.8 0:0 27.0	5 14 0 93

A Pyrex filter of coarse grade is satisfactory.